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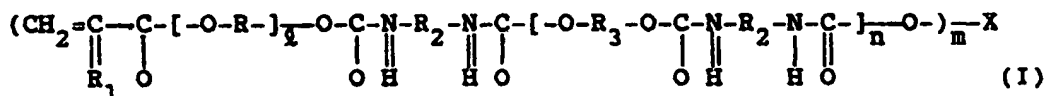
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Ultraviolet-curable Ink.

UV-curable inks for printing are provided which shrink little during curing, and exhibit good adhesion, conformability, aging-crack resistance, elasticity, elongation, tenacity, chemical resistance, and scratch resistance, and which comprise a UV-curing rubbery copolymer having the general formula



wherein R represents a C₂₋₈ alkylene group, R₁ represents H or CH₃, R₂ represents a diisocyanate residue, R₃ represents a residue of polyhydric alcohol, X is a moiety of dienic liquid rubber having one or more reactive hydroxyl groups, l is an integer from 1-4, m is a number from 1.0<m<3.0, and n is an integer from 1-12.

ULTRAVIOLET-CURABLE INK

The present invention relates to inks, particularly to ultraviolet (UV) curable inks for printing.

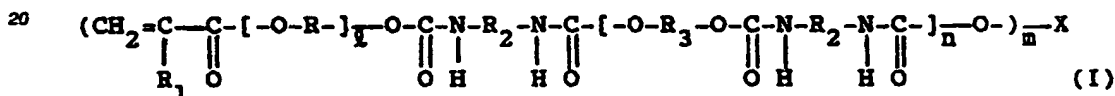
Many types of UV-curable ink are known, and which comprise a photo-oligomer, reactive diluent monomer, photo-initiator, photosensitiser, pigment, pigment dispersant, and other optional ingredients, such as flow adjusters, defoamers and levelling agents.

The known inks, when cured by UV irradiation, suffer from curing shrinkage so that adhesion deteriorates or is lost. Even when adhesion to the substrate is good, the substrate is frequently deformed, so that the cured ink loses conformability, and aging cracks may appear on standing, even with only a small impact of bending force.

The inks of the present invention do not suffer the above drawbacks and, in addition, possess superior adhesive properties and chemical resistance, and form stiff and tenacious coatings.

It has been discovered that the disadvantages of the prior art may be overcome by the inclusion of a UV-curable elastomeric copolymer in the ink. Such UV-curable copolymers have a high molecular weight and have a rubbery elastomer structure. It is generally desirable to further include a photopolymerisable monomer (photo-monomer) and/or a photopolymerisable oligomer (photo-oligomer) as a reactive diluent, and a photopolymerisation initiator (photo-initiator). The ink obtained is stiff and has good chemical resistance, low UV-curing shrinkage, as well as good post-cure elasticity and elongation.

The inks of the present invention are characterised in comprising a UV-curing rubbery copolymer having the general formula (I)



wherein R represents a C₂₋₈ alkylene group, R₁ represents H or CH₃, R₂ represents a diisocyanate residue, R₃ represents a residue of polyhydric alcohol, X is a moiety of dienic liquid rubber having one or more reactive hydroxyl groups, l is an integer from 1-4, m is a number from 1.0<m<3.0, and n is an integer from 1-12.

The amount of the compound of formula (I) used will vary according to requirements. Amounts of ingredients may also vary as required but, in general, can be specified in relation to the copolymer, taking 100 parts of the copolymer as a standard.

Thus, in a preferred aspect, the inks of the present invention further comprise, per 100 parts of copolymer, 50-500 parts of at least one kind of mono- or polyfunctional monomer; 0-300 parts of at least one kind of mono- or polyfunctional photopolymerisable oligomer; and 1-30 parts of a photopolymerisation initiator.

The UV-curable copolymer may be obtained by uniformly mixing and reacting: a dienic liquid rubber of about 1,000-10,000 MW and having one or more reactive hydroxyl groups; a diisocyanate compound, a polyhydric, preferably dihydric, alcohol having a molecular weight of up to about 300, and; a vinylic unsaturated monomer having at least one hydroxyl group.

Examples of suitable dienic liquid rubbers having a number average molecular weight of about 1,000-10,000 include 1,2-polybutadiene, 1,4-polybutadiene, 1,2-pentadiene, styrene-butadiene copolymers, acrylonitrile-butadiene copolymers and polyisoprene, which have at least one hydroxyl group in the molecule. These may be used alone or in admixture.

The valence (m) of hydroxyl groups in the molecule is about 1.0<m<3.0. If m≤1, the resultant rubbery copolymer tends to have a low photopolymerisation density and the photocured product or ink can be rather brittle. If m≥3, the photocured ink tends to be excessively hard and have poor elasticity.

Examples of suitable vinylic unsaturated monomers include, for example, 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylacrylate, 2-hydroxypropylmethacrylate and tripropyleneglycol-monomethacrylate, which may be used alone or in admixture.

Suitable dihydric alcohols include, for example, ethyleneglycol, diethyleneglycol, triethyleneglycol, 1,2-propyleneglycol, 1,3-propyleneglycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, dioxaneglycol (Trade Mark), trimethylolpropane-monoacrylate, trimethylolpropane-monoacrylate, trimethylolpropane-methacrylate and glycerol α-mono-allylether, which may be used alone or in admixture.

The components are advantageously mixed uniformly at a temperature preferably in the range of 40-

70°C, more preferably at 50-60°C, in an inert atmosphere such as nitrogen, to obtain the rubbery copolymer of formula (I).

Suitable photopolymerisable monomers for use in the present invention include mono- or polyfunctional polymers, such as acrylic or methacrylic esters of C₁-C₁₂ alcohol having a side chain, for example methacrylate, methylmethacrylate, ethacrylate, ethylmethacrylate, butylacrylate, butylmethacrylate, 2-ethylhexylacrylate, 2-ethylhexylmethacrylate, laurylacrylate or laurylmethacrylate; polyolpolyacrylates or polyolpolymethacrylates, such as trimethylolpropanediacrylate, trimethylolpropanetriacrylate, trimethylolpropanetrimethacrylate, neopentylglycoldiacrylate, or 1,6-hexanedioldimethacrylate; alkyl-substituted aminoalcohols or alkyl-substituted aminoalcoholmethacrylates, such as diethylaminoethylacrylate or diethylaminoethylmethacrylate; acrylamides or acrylimides, such as N-acryloylmorpholin; and N-vinyl-2-pyrrolidone, which may be used alone or in admixture.

The monomer(s) is mixed in an amount of 50-500 parts by weight with 100 parts by weight of the copolymer. If the amount of the photopolymerisable monomers is less than about 50 parts by weight, the viscosity of the ink will generally be too high. If the amount of the monomer exceeds 500 parts by weight, the desired rubbery elasticity of the ink may well not be attained.

Suitable optional photopolymerisable oligomers include epoxyacrylate series oligomers, polyesteracrylate series oligomers and urethaneacrylate series oligomers having at least 2 functionalities.

The photopolymerisable oligomer is mixed with the UV-curable copolymer in an amount of generally about 0-300 parts by weight, relative to 100 parts by weight of the rubbery copolymer. If the amount exceeds 300 parts by weight, elasticity of the ink may be impaired.

Many photopolymerisable monomers and oligomers, such as those listed above, are useful at low viscosity as photopolymerisable diluents.

Suitable photopolymerisation initiators include benzoin, benzoinalkylether, benzyldimethylketal, benzophenone, Michler's ketone, azisobutyronitrile, 1-azobis-1-cyclohexanecarbonitrile, naphthalenesulphonylchlorides, anthraquinones, biimidazoles, or thioxanthenes, which may be used alone or in admixture.

One or more of the initiators may be mixed with the copolymer generally in an amount of from about 1-30 parts by weight, relative to 100 parts by weight of the rubbery copolymer. If the amount of the initiator is less than 1 part by weight, the curing property of the ink is generally inferior. If the amount of the initiator exceeds 30 parts by weight, the cost of the ink is generally prohibitive.

Other components may optionally be used in the manufacture of inks according to the invention, such as sensitizers like tertiary amines, organic or inorganic pigments, pigment dispersants, flow adjusters affording suitable printability, defoamers, and levelling agents, as required.

Illustrative examples of sensitizers include 4-methylaminobenzoic acid isoamyl ester, and azidopyren, which may be used in an amount of 1-15 parts by weight relative to 100 parts by weight of copolymer.

Illustrative examples of pigment dispersants are polyamide, and salts of esters of polar acids and long chain polyaminoamides, which may be used in amounts of 0.1-4 parts by weight relative to 100 parts by weight of the rubbery copolymer.

Illustrative examples of flow adjusters are methylpolysiloxane, and modified acryl polymers, which may be used in an amount of 1-10 parts by weight relative to 100 parts by weight of the copolymer.

Illustrative examples of defoamers include hydrophobic polysiloxane/polyether copolymers, and compounds of dimethylpolysiloxane and silicic acid, which may be used in an amount of 1-10 parts by weight relative to 100 parts by weight of the copolymer.

Illustrative examples of levelling agents are polysiloxane/polyether copolymer, and modified organic polysiloxane, which may be used in an amount of 1-10 parts by weight relative to 100 parts by weight of the rubbery copolymer.

Pigments may be inorganic and/or organic, and may be used in an amount of 1-40 parts by weight relative to 100 parts by weight of the rubbery copolymer.

Mixing and dispersing may be effected by appropriate means such as a roller mill, to obtain a uniform UV-curable ink.

The UV-curable ink of the present invention adheres well to the substrate, shows no removal or peeling off from the join after stress, exhibits excellent conformability to the deformation of the substrate, and endures strong and rapid physical shocks, such as punching or bend processing of the substrate after printing.

The present invention will be illustrated in more detail with reference to the accompanying Examples, which are not to be construed as limiting on the present invention.

In the Examples, all quantitative measurements are by weight.

Examples 1-4

A UV-curable rubbery copolymer having the trade name of 12B-A or NU-A (photosensitive rubber "Mickelon UV" produced by Hayakawa Rubber Co.) was dissolved in N-vinyl-2-pyrrolidone (NVP - GAF Corp.) in the ratios shown in Table 1, added and mixed thoroughly with other raw materials, agitated, and blended twice on three rolls to obtain UV-curable inks.

The resulting inks were tested for screen printing, as follows.

Screen printing was effected by depicting a nega picture of an emulsion thickness of 10 μ m on a 250 mesh screen made of tetron, and printing the picture on a polycarbonate resin sheet of 0.5mm thickness.

The printed sheet was irradiated on a conveyer at a speed of 5 m/min with ultraviolet from 80 W/cm high pressure mercury vapor discharge lamps (such as type HMW 180 produced by Oak K.K.) at a distance of 120mm, to obtain a cured coating of a thickness of 8 μ m. The cured coating on the sheet was used at a test sample. The test samples were tested for adhesion by a tessellate plastic tape-peeling test, flexibility and elongation by a 180° bending test, and wear-resistance by a nail scratch test. Results are shown in Table 1.

Reference Examples 1-2

The procedures of Example 1 were repeated using ingredients as shown in Table 1, except that urethane-acrylate oligomer (trade name "Aronix M-1200") was used instead of the photosensitive rubber (trade name "12B-A" or "NU-A"). Results are shown in Table 1.

As will be appreciated from the foregoing description, the UV-curable ink of the present invention comprises the UV-curable rubbery copolymer of formula (I), so that the ink exhibits low shrinkage at the time of UV curing, good adhesion to the substrate, excellent conformability to bending or elongation of even particularly flexible substrates, superior scratch resistant properties, tenacious and/or abrasion resistant properties, and remarkably good resistance to corrosive chemical substances, such as acids or caustic materials.

Although the present invention has been illustrated with specific Examples, it is of course apparent to those skilled in the art that various changes and modifications thereof are possible without departing from the broad spirit and aspect of the present invention as defined in the appended claims.

Table 1(a)

Component	Example				Reference Example	
	1	2	3	4	1	2
(1) Photosensible rubber (12B-A)	100	100	-	-	-	-
(2) Photosensible rubber (NU-A)	-	-	100	100	-	-
(3) Urethaneacrylate oligomer (Aronix M-1200)	-	-	-	-	100	100
(4) N-vinyl-2-pyrrolidone	100	50	100	50	100	50
(5) Ethylcarbitolacrylate	50	100	50	100	50	100
(6) Trimethylolpropanetriacrylate	50	50	50	50	50	50
(7) Benzylidimethylketal	15	15	15	15	15	15
(8) Talc	20	20	20	20	20	20
(9) S-024	4	4	4	4	4	4
(10) Phthalocyanine blue	15	15	15	15	15	15
(11) Antiterro U	1	1	1	1	1	1
Total	370	370	370	370	370	370

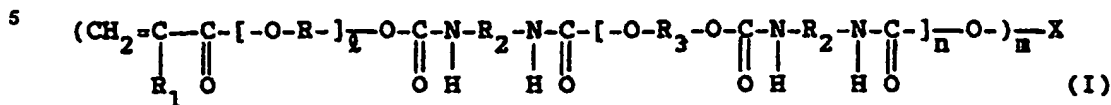
Table 1(b)

Test	Example				Reference Example	
	1	2	3	4	1	2
Tessellate plastic tape-peeling test	100/100	100/100	100/100	100/100	20/100	30/100
180° bending test	2 φ	2 φ	2 φ	2 φ	8 φ	8 φ
	good	good	good	good	cracked	deviation of coating from the sheet
Wear resistant property	good	good	good	good	peeled	damaged

Notes: (1) Mickelon UV, produced by Hayakawa Rubber Co. Ltd.
 (2) Mickelon UV, produced by Hayakawa Rubber Co. Ltd.
 (3) Produced by Toa Gosei Kagaku Kogyo
 (4) NVP, produced by GAF Inc.
 (5) EC-A, produced by Kyo-eisha Yushi Company
 (6) TMPTA, produced by Shin Nakamura Kagaku K.K.
 (7) Irgacure 651, produced by CIBA Geigy Co.
 (8) Mistron vapor talc, produced by Mistron Co.
 (9) Pigment, produced by Dainichi Seika Co.
 (10) Pigment dispersant, produced by BYK, Chemie Co.

Claims

1. A UV-curable ink comprising a compound of formula (I)



¹⁰ wherein R represents a C₂₋₈ alkylene group, R₁ represents H or CH₃, R₂ represents a diisocyanate residue, R₃ represents a residue of polyhydric alcohol, X is a moiety of dienic liquid rubber having one or more reactive hydroxyl groups, l is an integer from 1-4, m is a number from 1.0<m<3.0, and n is an integer from 1-12.

15 2. An ink according to claim 1 further comprising at least one mono- or polyfunctional monomer, and/or at least one mono- or polyfunctional photopolymerisable oligomer and a photopolymerisation initiator.

3. A UV-curable ink according to claim 1 or 2 comprising by weight; 100 parts of a UV-curable rubbery copolymer of formula (I); 50-500 parts of at least one kind of mono- or polyfunctional monomer; 0-300 parts of at least one kind of mono- or polyfunctional photopolymerisable oligomer; and 1-30 parts of a photopolymerisation initiator.

4. An ink according to any preceding claim wherein R_3 represents a residue of a dihydric alcohol.

5. An ink according to any preceding claim further comprising at least one of the following types of Ingredient: pigment; pigment dispersant; flow adjuster; defoamer, and; levelling agent.

6. A UV-curable ink comprising a UV-curable elastomeric copolymer.